

# PATENT SPECIFICATION

(11) 1372374

1372374

- (21) Application No. 54654/71 (22) Filed 24 Nov. 1971  
 (31) Convention Application No. 93856 (32) Filed 30 Nov. 1970 in  
 (33) United States of America (US)  
 (44) Complete Specification published 30 Oct. 1974  
 (51) International Classification C08F 1/18 1/24//B44D 1/50 C08F 1/20  
 (52) Index at acceptance



C3P 14D2F 14D2G2 14D3C1 14D3C3 14D3C4 14D6  
 14D8 14D9 14K11 14K7 14K8 14P1X 14P4C 14P5  
 14P6C 14P6D 14P6H 14P6X 8D2A 8D5 8P5 8P6C  
 8P6D 8P6H 8P6X D1  
 B2E 19Y 20Y 30Y 30Z 309 359 38X 38Y 418 41X 41Y 428  
 44Y 456 467 498 507 50Y 52X

## (54) CURING OF FILM BY EXPOSURE TO ULTRAVIOLET LIGHT

(71) We, WEYERHAEUSER COMPANY, a corporation organized and existing under the laws of the State of Washington, United States of America, of Tacoma Building, Tacoma, Washington, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—  
 It is known that many polymerizable systems can be cured by exposing them to ionizing radiation. The use of ionizing radiation, and particularly electron beam radiation, has a number of distinct advantages over conventional methods of effecting polymerization and cross-linking using catalytic agents, especially when used to cure film coatings on wood and wood products, fabrics, rubber, glass, metal and similar substances. For example, it avoids the sometimes lengthy induction period associated with catalyst-induced curing, enables the use of film-forming compositions having indefinite pot lives, produces little temperature rise during polymerization, and produces, in many cases, a superior coating-to-substrate bond. Many films can be cured in less than one second using high-energy electrons. Unfortunately, however, if the uncured film is allowed to come into contact with air, oxygen inhibition of ionizing radiation curing often results in the surface or surfaces of the film being tacky or otherwise not as well cured as the bulk of the film. Although the uncured material is present only in a very thin layer, i.e., of the order of from  $1 \times 10^{-3}$  to  $1 \times 10^{-4}$  inch, this is sufficient to cause serious losses of coating gloss and problems with scratching. When the film is in the form of a coating on articles such as wood panels, blocking can occur when the articles are stored in a stacked relationship.

Undercured surfaces caused by oxygen inhibition can usually be avoided by covering the uncured film with an inert cover sheet or by maintaining the film in an oxygen-free atmosphere until curing is effected. These techniques, however, are often impractical or too expensive for commercial operations.

It has now been found that undercured surfaces of film resulting from oxygen inhibition of curing by ionizing radiation can be eliminated by exposure thereof to ultraviolet light.

Thus, according to the present invention, there is provided a method of advancing the state of cure of a surface layer of a polymeric film derived from polymerisable material which is curable by exposure to ionizing radiation, which film has been obtained by exposing a film of said polymerisable material to ionizing radiation in the presence of oxygen which has inhibited the cure of said surface layer, said method comprising exposing said surface layer to ultraviolet light.

Using a high-intensity source of ultraviolet light, this ordinarily can be accomplished by exposure for less than one minute. Quite surprisingly, undercured surfaces can be rapidly eliminated by exposure to ultraviolet light even in the absence of free radical catalysts or photo-initiators in the film.

A particularly advantageous system for the rapid and complete curing of polymerisable films results from the combination of an electron beam and ultraviolet light. Through the use of the former, the curing of relatively thick and opaque films can be accomplished so rapidly that no bubbling of volatile components and no excessive absorption of the uncured film into porous substrates can occur. The thin undercured surface layer which ordinarily remains is easily penetrated and rapidly cured by the ultraviolet light.

The method of this invention is applicable

[Price 25p]

to any polymerisable film which upon being exposed to ionizing radiation is cured to the desired degree except for a thin uncured surface layer resulting from oxygen inhibition of polymerisation induced by ionizing radiation. In general, such compositions include those which are polymerisable through free radical mechanisms.

One preferred class of such compositions comprises polymerisable resins having terminal acrylate or methacrylate groups and disclosed in our copending application No. 18925/69, Serial No. 1256781. These resins can be prepared by (1) reacting a polyfunctional material selected from dicarboxylic acids having from 3 to 15 carbon atoms and ester-forming derivatives thereof with a 2-hydroxyalkyl acrylate or 2-hydroxyalkyl methacrylate or (2) reacting a half-ester of a 2-hydroxyalkyl acrylate or 2-hydroxyalkyl methacrylate and a dicarboxylic acid having from 3 to 15 carbon atoms with a polyepoxide having reactive glycidyl groups.

Another preferred class comprises polymerisable resins having terminal acrylate or methacrylate groups and prepared by reacting a polyisocyanate having terminal reactive isocyanate groups with a 2-hydroxyalkyl acrylate or 2-hydroxyalkyl methacrylate.

These classes of polymerisable resins can be used undiluted or dissolved in up to 50% by weight of a monomer containing terminal  $>C=C<$  unsaturation.

Other compositions useful in the method of this invention are the alpha-beta, olefinically unsaturated organic resins disclosed in United States Patent 3,437,514. These include unsaturated polyester resin, acrylic resins, modified acrylic resin, urethane-modified organic resin, silicone-modified organic resins, and epoxy resins.

Monomers containing terminal  $>C=C<$  unsaturation in which the above-mentioned resins can be dissolved include, for example, monovinyl aromatic hydrocarbons of the benzene series such as styrene, vinyl toluene, ethyl vinyl benzene, isopropyl styrene, tert-butyl styrene, sec-butyl styrene and mixtures thereof,  $\alpha$ -methyl styrene; divinyl compounds of the benzene series such as divinyl benzene; acrylic acid, vinyl acetate, diacetone acrylamide, methyl methacrylate, ethyl methacrylate, n-butyl acrylate, ethyl acrylate, cyclohexyl acrylate and  $\beta$ -hydroxyethyl acrylate.

The expression "ionizing radiation" as used herein is intended to include both particulate radiation, such as highly accelerated electrons, protons, neutrons, alpha particles, deuterons and beta particles, and electromagnetic radiation such as x-rays and gamma rays. The dose of ionizing radiation necessary to cure a given film will depend on the dose rate, temperature, and thickness and composition of the film. Effective results are

obtained, for example, by using high energy electrons of from 20,000 to 10,000,000 electron volts and dose rates of from 1 megarad per minute to 10 megarads per second. The use of an electron beam of sufficient voltage and intensity to penetrate the full thickness of the film and to effect curing in several seconds or less is preferred.

Any type of ultraviolet light source including shortwave fluorescent lamps, longwave fluorescent lamps, mercury vapor lamps, and even sunlight can be used to effect surface cure. Shortwave sources, however, eliminate uncured surfaces much more rapidly than do longwave sources. High-intensity quartz mercury-vapor arc lamps are especially preferred where speed of surface cure is of importance. Intensities in the range of from 5 to 15 watts per square inch per minute are preferred, but lower intensities can be used if longer cure times can be tolerated. The length of exposure to ultraviolet light necessary to effect surface cure depends on the intensity of the ultraviolet light source, the degree to which the surface is uncured, and the composition of the film. Surfaces exposed about three inches below a 1200-watt quartz mercury-vapor lamp can ordinarily be cured to the desired degree in from two to twenty seconds.

As noted previously, rapid surface curing using ultraviolet light can be readily achieved in the absence of any free radical catalyst or photo-initiator. In some instances, however, the addition of free radical generating catalysts, e.g. benzoyl peroxide and azo-bis-isobutyronitrile, or photo-initiators e.g. benzoin and 2,3-butanedione may enable even more rapid elimination of uncured surfaces. Energy in the visible range from unfiltered ultraviolet light sources is also more effective when such photo-initiators are present.

The method of this invention is especially well suited for the curing of films in the form of clear coatings on hardwood, plywood panels, particleboard, overlaid softwood plywood, solid fiberboard and paper carton board and for the curing of pigmented coatings (containing, for example, titanium dioxide, calcium carbonate, zinc oxide or talc) on wood siding, hardboard, plywood, steel, tin and aluminium. This method is also well suited for the curing of unsupported films and the curing of surfaces of porous materials impregnated with ionizing radiation-curable liquids. For example, impregnated paper and wood can be cured by this method to produce paper-plastic and wood-plastic combinations.

The following examples are provided by way of illustration and are not intended to be in any way limiting of the invention. All parts are by weight unless otherwise indicated.

#### EXAMPLE 1

A coating formulation is prepared by dis-

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solving 20 parts of butyl acrylate in 80 parts of a vinyl ester resin prepared by reacting the half-ester condensation product of 2 moles 2 - hydroxyethyl acrylate and 2 moles maleic anhydride with 1 mole bisphenol A diglycidyl ether. A 0.003-inch coating of this formulation is spread on the surface of hardboard siding. The coated siding is then passed two times at 50 feet per minute under an electron beam operating at 300,000 volts and 20 milliamperes. The beam has an 18-inch scan and the total dosage is 8.5 megarads. The coating has cured hard but the surface is slightly tacky and can be readily scratched. The coating is then exposed to a 100-watt quartz mercury lamp at a distance of 1-1/2 inches with no filter for a period of 30 seconds. After cooling, the surface has no trace of tackiness and does not leave a white mark when scratched with a coin.

#### EXAMPLE 2

A 0.005-inch coating of a formulation similar to that of Example 1, but consisting of 25 parts of n - butyl acrylate and 75 parts of the vinyl ester resin used in Example 1, is drawn on plywood and subjected to electron beam irradiation as in Example 1. The coating has again cured hard but has a tacky surface. The coated board is then passed at a distance of three inches and at a rate of 20 feet per minute under a 12-inch long, 1200-watt Hanovia (Registered Trade Mark) quartz mercury-arc lamp having a 4-inch wide reflector. After five successive passes, the surface is tack-free but still leaves a white mark on scratching. After five additional passes (for a total exposure of 10 seconds under the reflector) the surface no longer leaves a white scratch mark and exhibits the same hardness properties as an identical coating cured in contact with a covering film of polyethylene terephthalate to prevent surface-cure-inhibition by oxygen.

#### EXAMPLE 3

To the coating formulation of Example 2 is added one part glycidyl acrylate and 0.5 part of benzoin. After being cured by an electron beam as in Example 1 the coating is cured hard but the surface is tacky. After being passed under the 1200-watt lamp described in Example 2 five times at a rate of 20 feet per minute (for a total exposure of 5 seconds), the surface is tack-free and does not give a white mark upon scratching.

#### EXAMPLE 4

A coating consisting of (a) 17.5 parts of a vinyl ester resin produced by reacting the half-ester condensation product of 2 moles 2-hydroxyethyl acrylate and 2 moles maleic anhydride with 1 mole bisphenol A diglycidyl ether, (b) 17.5 parts of a vinyl ester resin produced by reacting the half-ester condensa-

tion product of 2 moles 2 - hydroxypropyl acrylate and 2 moles maleic anhydride with 1 mole butanediol diglycidyl ether, (c) 15 parts n - butyl acrylate, (d) 30 parts titanium dioxide and (e) 20 parts of talc is spread on plywood and irradiated under an electron beam as in Example 1. The hard, resilient, white coating obtained has a tacky surface which is then cured to a tack-free state by passing it six times at 60 feet per minute (a total of 2 seconds exposure) under the 1200-watt lamp described in Example 2.

#### EXAMPLE 5

A conventional unsaturated polyester resin, Polyite (Registered Trade Mark) 31-583 (a semi-rigid unsaturated polyester dissolved in vinyl toluene—Reichhold Chemical Co.), is spread on metal foil at a thickness of 0.005-inch. After three passes under the electron beam as in Example 1 at 60 feet per minute the film will snap break upon bending but is very tacky on the surface. After 10 passes under the 1200-watt lamp described in Example 2 at a rate of 20 feet per minute (a total of 10 seconds exposure), the surface was hard and free of tack.

#### EXAMPLE 6

A resin solution is prepared by reacting 100 parts polypropylene glycol (molecular weight 400), 78.2 parts tolylene diisocyanate, 91 parts 2 - hydroxyethyl acrylate and 0.2 parts tin octoate at 60°C. A 0.004-inch thick coating is spread onto carton board and the coating is irradiated by passing the board three times at 84 ft. per min. under the electron beam as in Example 1. The total dose is 6 megarads. The resulting clear coating is flexible and firm, but has a tacky surface. The board is passed five times under the ultraviolet light as in Example 2 to give a tack-free coating.

#### EXAMPLE 7

Example 6 is repeated with the modification that a 0.007-inch coating is applied. Identical results are obtained.

#### EXAMPLE 8

The pigmented coating mix of Example 4 with 0.5% benzoin added is spread on overlaid plywood at a thickness of 0.011 inch. The coating is irradiated as in Example 1 at 60 ft. per min. for three passes to give a hard but tacky coating. After five passes at 20 ft. per min. under the ultraviolet lamp as in Example 2, the surface is tack-free and is not scratched by a coin.

#### EXAMPLE 9

Example 8 is repeated with the modification that the hard but tacky coating obtained after irradiation is passed at a distance of three inches under a 12-inch, 1800-watt

5 "Chromolux" infra-red lamp having a four inch wide reflector. After ten passes under the lamp at 60 ft. per min., there is no reduction of surface tackiness. Continuous exposure of the coating under the lamp for several seconds results in darkening of the surface without eliminating tackiness.

WHAT WE CLAIM IS:—

10 1. A method of advancing the state of cure of a surface layer of a polymeric film derived from polymerisable material which is curable by exposure to ionizing radiation, which film has been obtained by exposing a film of said polymerisable material to ionizing radiation in the presence of oxygen which has inhibited the cure of said surface layer, said method comprising exposing said surface layer to ultraviolet light.

20 2. A method of curing a film of polymerisable material that is curable by exposure to ionizing radiation, said method comprising exposing the film to ionizing radiation in the presence of oxygen which inhibits the cure of the surface layer of the film and there-  
25 after exposing the film to ultraviolet light to advance the state of cure of the surface layer.

3. A method as claimed in claim 1 or claim 2 in which the ionizing radiation is an electron beam.

4. A method as claimed in any of claims 1 to 3 wherein the source of said ultraviolet light is a quartz mercury-vapour arc lamp.

5. A method as claimed in any of claims 1 to 4 wherein said film is a coating on a substrate.

6. A method as claimed in any of claims 1 to 5 wherein said film contains a photo-initiator.

7. A method as claimed in claim 6 wherein said photo-initiator is benzoin.

8. A method as claimed in claim 1 substantially as hereinbefore described and as shown in the Examples.

9. A method as claimed in claim 2, substantially as hereinbefore described and as shown in the Examples.

10. A cured product obtained by the process of any of claims 1 to 9.

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10 Fleet Street,  
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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1974.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.